

# Isotope Effects on Hydride Transfer Reactions from Transition Metal Hydrides to Trityl Cation. An Inverse Isotope Effect for a Hydride Transfer

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**Abstract:** Hydride transfer from transition metal hydrides (MH) to  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  gives  $\text{M}-\text{FBF}_3$  and  $\text{Ph}_3\text{CH}$ . Deuterium kinetic isotope effects were determined for several MH/MD pairs ( $\text{CH}_2\text{Cl}_2$  solution, 25 °C). For hydride transfer from  $\text{Cp}^*(\text{CO})_3\text{MoH}$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) to substituted trityl cations containing zero, one, two, or three *p*-MeO groups [ $\text{Ph}_n(\text{p-MeOC}_6\text{H}_4)_{3-n}\text{C}^+\text{BF}_4^-$ ;  $n = 3, 2, 1, 0$ ], the isotope effect remains essentially constant at  $k_{\text{MoH}}/k_{\text{MoD}} = 1.7\text{--}1.9$  as the rate constant decreases from  $k_{\text{H}^-} = 6.5 \times 10^3$  to  $1.4 \text{ M}^{-1} \text{ s}^{-1}$ . For hydride transfer to  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  from five metal hydrides [ $\text{Cp}(\text{CO})_3\text{MoH}$ ,  $\text{Cp}^*(\text{CO})_3\text{WH}$ , (indenyl)( $\text{CO})_3\text{WH}$ ,  $\text{Cp}^*(\text{CO})_3\text{MoH}$ , and *trans*- $\text{Cp}(\text{CO})_2(\text{PCy}_3)\text{MoH}$ ;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ] with second-order rate constants  $k_{\text{H}^-} \geq 3.8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , the kinetic isotope effects are also  $k_{\text{MH}}/k_{\text{MD}} = 1.7\text{--}1.8$ . For a series of five tungsten hydrides with substituted Cp ligands, the kinetic isotope effects decrease from  $k_{\text{WH}}/k_{\text{WD}} = 1.8$  to 0.47 as the rate constant decreases (from  $k_{\text{H}^-} = 2.0 \times 10^3$  to  $0.72 \text{ M}^{-1} \text{ s}^{-1}$ ). The steadily decreasing values of  $k_{\text{MH}}/k_{\text{MD}}$  with decreasing rate constants of hydride transfer are interpreted as indicating progressively stronger force constants of isotopically sensitive modes of the transition state, as the reaction slows down in progressing from more electron-donating Cp ligands to less electron-rich Cp ligands. The inverse isotope effect ( $k_{\text{WH}}/k_{\text{WD}} = 0.47$ ) found for the slowest tungsten hydride,  $(\text{C}_5\text{H}_4\text{CO}_2\text{Me})(\text{CO})_3\text{WH}$ , is proposed to be due to a product-like transition state for irreversible hydride transfer.

## Introduction

Kinetic isotope effects<sup>1–3</sup> are useful in mechanistic studies, since they can provide insight into the transition state of the reaction being examined. Hydride ( $\text{H}^-$ ) transfer reactions between carbons are pertinent to the chemistry of nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ) analogues.<sup>4</sup> Kinetic and mechanistic studies have established details of hydride transfers from 1,4-dihydropyridines and related hydride donors to carbon-based hydride acceptors such as pyridinium or acridinium cations. Kreevoy and co-workers reported experimental data and calculations for hydride transfers between a variety of  $\text{NAD}^+$  analogues,<sup>5</sup> and a thorough analysis of kinetic isotope effects<sup>6</sup> played a key role in the development of an understanding of these hydride transfers.

Ionic hydrogenations of organic substrates involve stepwise addition of  $\text{H}_2$ , in the form of a proton transfer followed by a

hydride transfer. The utility of such reactions in organic synthetic reactions is well-established,<sup>7</sup> with the acid typically being  $\text{CF}_3\text{-CO}_2\text{H}$  and silanes such as  $\text{HSiEt}_3$  serving as the hydride donor. We have shown that ionic hydrogenations using transition metal hydrides as the hydride donor can be utilized in the hydrogenation of alkenes,<sup>8</sup> alkynes,<sup>9</sup> aldehydes<sup>10</sup> and ketones.<sup>10</sup> Related reactions were shown<sup>11</sup> to produce ether complexes of tungsten from the reaction of acetals with  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{Cp}(\text{CO})_3\text{WH}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ).

We recently reported<sup>12</sup> a detailed study of the kinetics of hydride transfer from a series of metal hydrides to  $\text{Ph}_3\text{C}^+$ . The rate constants for kinetic hydricity spanned a range of greater than  $10^6$ . Studies of isotope effects in organometallic chemistry have been especially beneficial in understanding the reactivity of transition metal hydrides.<sup>13</sup> In this paper, we report kinetic isotope effects on the reaction of metal hydrides with  $\text{Ph}_3\text{C}^+$ . For a series of tungsten hydrides with systematically varied substituted cyclopentadienyl ligands, the isotope effects pro-

(1) (a) Bigeleisen, J. *J. Chem. Phys.* **1949**, *17*, 675–678. (b) Bigeleisen, J.; Wolfsberg, M. *Adv. Chem. Phys.* **1958**, *1*, 15–76.

(2) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; John Wiley and Sons: New York, NY, 1980; (a) pp 29–36, (b) pp 44–45, 71, 154–156, (c) pp 32, 69, 130, 140.

(3) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265–273.

(4) For a review of mechanistic studies of hydride transfer from 1,4-dihydropyridines, see: Bunting, J. W. *Bioorg. Chem.* **1991**, *19*, 456–491.

(5) (a) Kreevoy, M. M.; Ostović, D.; Lee, I.-S. H.; Binder, D. A.; King, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 524–530. (b) Lee, I.-S. H.; Ostović, D.; Kreevoy, M. *J. Am. Chem. Soc.* **1988**, *110*, 3989–3993. (c) Lee, I.-S. H.; Jeong, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1997**, *119*, 2722–2728.

(6) (a) Kreevoy, M. M.; Kotchevar, A. T. *J. Am. Chem. Soc.* **1990**, *112*, 3579–3583. (b) Kim, Y.; Truhlar, D. G.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 7837–7847. (c) Kim, Y.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 7116–7123.

(7) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633–651.

(8) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602–8612.

(9) Luan, L.; Song, J.-S.; Bullock, R. M. *J. Org. Chem.* **1995**, *60*, 7170–7176.

(10) Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233–1235.

(11) Song, J.-S.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 11134–11141.

(12) Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121–13137.

(13) For a review of isotope effects in reactions of metal hydrides, see: Bullock, R. M. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, NY, 1992; Chapter 8, pp 263–307.

**Table 1.** Kinetic Isotope Effects and Rate Constants<sup>a</sup> for Hydride Transfer from Metal Hydrides to Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> (CH<sub>2</sub>Cl<sub>2</sub>, 25 °C)

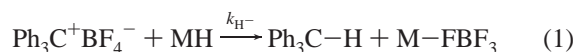
metal hydride	$k_{MH}/k_{MD}$	$k_H^-$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup>
(C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> Me)(CO) <sub>3</sub> WH	0.47	$7.2 \times 10^{-1}$
Cp(CO) <sub>3</sub> WH	0.92	$7.6 \times 10^1$
(C <sub>5</sub> H <sub>4</sub> Me)(CO) <sub>3</sub> WH	1.4	$2.5 \times 10^2$
Cp*(CO) <sub>3</sub> WH	1.7	$1.9 \times 10^3$
(Indenyl)(CO) <sub>3</sub> WH	1.8	$2.0 \times 10^3$
Cp(CO) <sub>3</sub> MoH	1.8	$3.8 \times 10^2$
Cp*(CO) <sub>3</sub> MoH	1.7	$6.5 \times 10^3$
<i>trans</i> -Cp(CO) <sub>2</sub> (PCy <sub>3</sub> )MoH	1.7	$4.3 \times 10^5$

<sup>a</sup> ±10% estimated uncertainty for all rate constants. <sup>b</sup> Rate constants reported in ref 12.

gressed from normal ( $k_{WH}/k_{WD} = 1.8$ ) to inverse ( $k_{WH}/k_{WD} = 0.47$ ) as the rate constants decreased.

## Results and Discussion

The kinetics of hydride transfer from metal hydrides to Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> (eq 1) were reported recently.<sup>12</sup> Stopped-flow



techniques were used for most of these measurements, with conventional UV–vis monitoring being employed for the slower reactions. An excess of metal hydride was used, and the rate of disappearance of [Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup>] was cleanly first order. Plots of observed pseudo-first-order rate constants ( $k_{\text{obs}}$ ) vs [MH] were linear, establishing the second-order rate law:  $-d[\text{Ph}_3\text{C}^+\text{BF}_4^-]/dt = k_H^-[\text{Ph}_3\text{C}^+\text{BF}_4^-][\text{MH}]$ . The deuterium isotope effects were determined by comparison of rate constants found for metal hydrides (MH) and their corresponding metal deuterides (MD). These kinetic isotope effects ( $k_{MH}/k_{MD}$ ) are shown in Table 1, along with the rate constants ( $k_H^-$ ) for hydride transfer.

For five hydrides [Cp(CO)<sub>3</sub>MoH, Cp\*(CO)<sub>3</sub>WH, (indenyl)(CO)<sub>3</sub>WH, Cp\*(CO)<sub>3</sub>MoH, and *trans*-Cp(CO)<sub>2</sub>(PCy<sub>3</sub>)MoH; Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>] with second-order rate constants  $k_H^- \geq 3.8 \times 10^2$  M<sup>-1</sup> s<sup>-1</sup> for hydride transfer to Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup>, the kinetic isotope effects are essentially invariant:  $k_{MH}/k_{MD} = 1.7$ – $1.8$ . These isotope effects are similar to the value of  $k_{SiH}/k_{SiD} = 1.49$  found for hydride transfer from (H/D)SiMe<sub>2</sub>Ph to Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>-</sup> (CH<sub>2</sub>Cl<sub>2</sub>, 25 °C)<sup>14</sup> and to the  $k_{SiH}/k_{SiD} = 1.68$  found for hydride transfer from (H/D)SiEt<sub>3</sub> to (MeOC<sub>6</sub>H<sub>4</sub>)(Ph)CH<sup>+</sup> (CH<sub>2</sub>Cl<sub>2</sub>, -70 °C).<sup>15</sup> Kinetic isotope effects for all of these *hydride* transfers to trityl cations are less than those reported recently by Norton's group,<sup>16</sup> for *hydrogen atom* transfers from metal hydrides to a substituted trityl radical.<sup>17</sup> A kinetic isotope effect of  $k_{MnH}/k_{MnD} = 3.2$  was found at 25 °C for hydrogen atom transfer from HMn(CO)<sub>5</sub>/DMn(CO)<sub>5</sub> to (*p*-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C•. A larger kinetic isotope effect was measured for hydrogen atom transfer from H<sub>2</sub>O<sub>8</sub>(CO)<sub>4</sub>/D<sub>2</sub>O<sub>8</sub>(CO)<sub>4</sub> ( $k_{OH}/k_{OD} = 4.3$ ).<sup>16</sup>

The effect of progressive deactivation of Ph<sub>3</sub>C<sup>+</sup> by substitution with *p*-MeO groups was examined for hydride transfer from Cp\*(CO)<sub>3</sub>Mo(H/D). Table 2 shows that, while the rate constants for hydride transfer decrease from  $k_H^- = 6.5 \times 10^3$  to  $1.4 \text{ M}^{-1}$

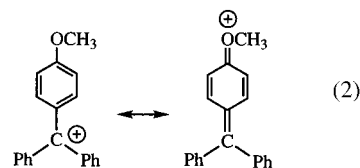
**Table 2.** Kinetic Isotope Effects and Rate Constants<sup>a</sup> for Hydride Transfer from Cp\*(CO)<sub>3</sub>MoH to Ph<sub>*n*</sub>(*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3-*n*</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> (*n* = 3, 2, 1, 0) (CH<sub>2</sub>Cl<sub>2</sub>, 25 °C)

trityl cation	$k_{MoH}/k_{MoD}$	$k_H^-$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup>
Ph <sub>3</sub> C <sup>+</sup>	1.7	$6.5 \times 10^3$
Ph <sub>2</sub> ( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> )C <sup>+</sup>	1.8	$1.4 \times 10^2$
Ph( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> C <sup>+</sup>	1.9	$1.1 \times 10^1$
( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> C <sup>+</sup>	1.9	$1.4 \times 10^0$

<sup>a</sup> ±10% estimated uncertainty for all rate constants. <sup>b</sup> Rate constants reported in ref 12.

s<sup>-1</sup> as the number of stabilizing *p*-MeO groups increases, the kinetic isotope effect exhibits little change ( $k_{MoH}/k_{MoD} = 1.7$ – $1.9$ ). Mayr and co-workers previously reported<sup>15</sup> that kinetic isotope effects for hydride transfers from (H/D)SiPh<sub>3</sub> were similarly insensitive to the hydride transfer rate constant. Hydride transfer to (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sup>+</sup> had an isotope effect of  $k_{SiH}/k_{SiD} = 2.14$ , compared to  $k_{SiH}/k_{SiD} = 2.07$  for hydride transfer to (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sup>+</sup>, despite a relative rate constant ratio of about 5000 for the hydride transfers.<sup>15</sup> A larger range of kinetic isotope effects was found ( $k_H/k_D = 1.8$ – $3.2$ ) for hydride transfer from formate (HCO<sub>2</sub><sup>-</sup>/DCO<sub>2</sub><sup>-</sup>) to a series of triarylcarbenium ions.<sup>18</sup>

The MeO groups provide significant electronic stabilization of the trityl cation, due to resonance forms such as those shown in eq 2. The difference in rate constants could be due to the



MeO-substituted trityl cations having an increased barrier to attaining the proper geometry for the transition state for hydride transfer. An increasing number of stabilizing MeO groups will raise the barrier for the structural and electronic reorganization required to progress from a ground state that is planar<sup>19</sup> about the central (sp<sup>2</sup>) carbon, to the more pyramidalized geometry expected at carbon for the transition state for hydride transfer. If these differences in reorganization energy of the substituted trityl cations are the predominant factor contributing to the overall change in the barriers for the reaction, then the barrier for the actual hydride transfer step could be similar for all of these MeO-substituted trityl cations, thus accounting for negligible change in kinetic isotope effect.

Deuterium kinetic isotope effects were measured for a systematically varied series of five tungsten hydrides/deuterides, as shown in the top part of Table 1. In contrast to the nearly invariant isotope effects found above when the hydride *acceptor* changed, there is a clear trend that the isotope effects decrease with decreasing rate constants as the tungsten hydride is changed. For the two most hydridic tungsten hydrides, Cp\*(CO)<sub>3</sub>WH and (indenyl)(CO)<sub>3</sub>WH,  $k_{MH}/k_{MD} = 1.7$ – $1.8$  (Figure 1). A diminished  $k_{MH}/k_{MD}$  of 1.4 is found for (C<sub>5</sub>H<sub>4</sub>Me)(CO)<sub>3</sub>W(H/D), and the isotope effect ( $k_{MH}/k_{MD} = 0.92$ ) found for Cp(CO)<sub>3</sub>W(H/D) is displayed in Figure 2. The most unusual observation is the inverse isotope effect,  $k_{MH}/k_{MD} = 0.47$ , determined for the least hydridic complex, (C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me)(CO)<sub>3</sub>W(H/D), as shown in Figure 3.

(18) Stewart, R.; Toone, T. W. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1243–1248.

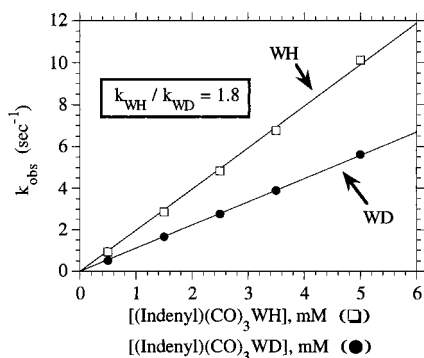
(19) The crystal structure of Ph<sub>3</sub>C<sup>+</sup> shows it to be planar about the central carbon: Gomes de Mesquita, A. H.; MacGillavry, C. H.; Eriks, K. *Acta Crystallogr.* **1965**, *18*, 437–443.

(14) Chojnowski, J.; Fortuniak, W.; Stanczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776–7781.

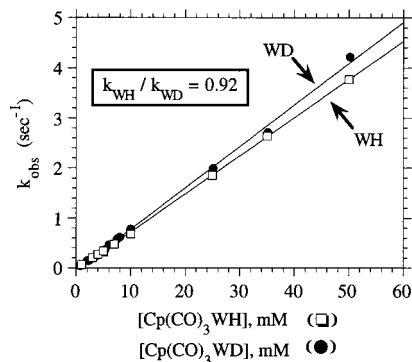
(15) Mayr, H.; Basso, N.; Hagen, G. *J. Am. Chem. Soc.* **1992**, *114*, 3060–3066.

(16) Rodkin, M. A.; Abramo, G. P.; Darula, K. E.; Ramage, D. L.; Santora, B. P.; Norton, J. R. *Organometallics* **1999**, *18*, 1106–1109.

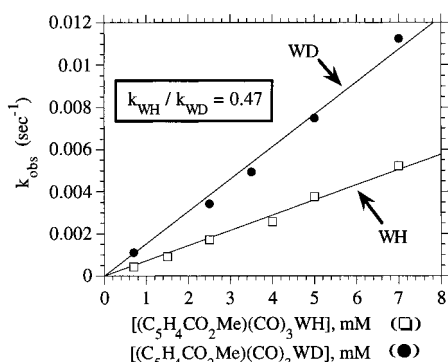
(17) (a) For an informative comparison of proton, hydrogen atom and hydride transfer reactions in organic systems, including a discussion of kinetic isotope effects, see: Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic Press: New York, NY, 1985; Chapter 4. (b) Page 160 of ref 17a.



**Figure 1.** Plot of  $k_{\text{obs}}$  vs (indenyl)(CO)<sub>3</sub>WH (□) and (indenyl)(CO)<sub>3</sub>WD (●) for reaction with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.



**Figure 2.** Plot of  $k_{\text{obs}}$  vs Cp(CO)<sub>3</sub>WH (□) and Cp(CO)<sub>3</sub>WD (●) for reaction with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.



**Figure 3.** Plot of  $k_{\text{obs}}$  vs (C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me)(CO)<sub>3</sub>WH (□) and (C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me)(CO)<sub>3</sub>WD (●) for reaction with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.

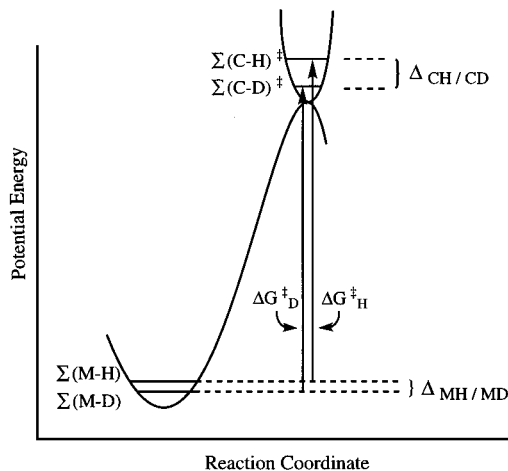
The second-order rate constant ( $k_{\text{H}}^- = 53 \text{ M}^{-1} \text{ s}^{-1}$ ) found<sup>12</sup> for hydride transfer from Cp(CO)<sub>3</sub>WH to Ph<sub>3</sub>C<sup>+</sup>BAR'<sub>4</sub><sup>-</sup> [Ar' = 3,5-bis(trifluoromethyl)phenyl] is somewhat smaller than that found for reaction of the same hydride with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> ( $k_{\text{H}}^- = 76 \text{ M}^{-1} \text{ s}^{-1}$ ). The kinetic isotope effect ( $k_{\text{WH}}/k_{\text{WD}} = 0.81$ ) found for reaction of Ph<sub>3</sub>C<sup>+</sup>BAR'<sub>4</sub><sup>-</sup> with Cp(CO)<sub>3</sub>W(H/D) is similar to that found ( $k_{\text{WH}}/k_{\text{WD}} = 0.92$ ) with Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup>, indicating a negligible effect of the counterion on the isotope effect.

Stretching frequencies  $\nu(\text{M}-\text{H})$  and  $\nu(\text{M}-\text{D})$  of the tungsten hydrides and deuterides used in this study were measured by IR spectroscopy and are listed in Table 3, along with the  $\nu(\text{CO})$  bands of the metal carbonyls. Substitution of the  $\nu(\text{M}-\text{H})$  and  $\nu(\text{M}-\text{D})$  bands of Cp(CO)<sub>3</sub>WH into eq 3 gives  $k_{\text{MH}}/k_{\text{MD}} = 3.5$  as the maximum semiclassical isotope effect.

$$\frac{k_{\text{MH}}}{k_{\text{MD}}} = \exp\left\{\frac{hc}{2k_{\text{B}}T}(\bar{\nu}_{\text{MH}} - \bar{\nu}_{\text{MD}})\right\} \quad (3)$$

**Table 3.** IR Data (cm<sup>-1</sup>, Hexane Solution) of W-H and W-D Complexes

tungsten hydride	$\nu_{\text{MH}}$	$\nu_{\text{MD}}$	$\nu_{\text{CO}}$
(C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> Me)(CO) <sub>3</sub> WH	1847 (w)	1328 (w)	2033 (s), 1945 (vs)
Cp(CO) <sub>3</sub> WH	1845 (w)	1326 (w)	2026 (s), 1938 (vs)
(C <sub>5</sub> H <sub>4</sub> Me)(CO) <sub>3</sub> WH	1843 (w)	1322 (w)	2023 (s), 1935 (vs)
Cp*(CO) <sub>3</sub> WH	1827 (w)	1311 (w)	2013 (s), 1924 (vs)
(indenyl)(CO) <sub>3</sub> WH	1854 (w)	1333 (w)	2024 (s), 1940 (vs)



**Figure 4.** Qualitative energy level diagram for a reaction where an M-H(D) bond is cleaved and a C-H(D) bond is formed. The inverse kinetic isotope effect ( $k_{\text{MH}}/k_{\text{MD}} < 1$ ) is a result of the collective relative zero-point energy differences ( $\Delta_{\text{CH/CD}} > \Delta_{\text{MH/MD}}$ ).

Norton and co-workers reported<sup>20</sup>  $k_{\text{WH}}/k_{\text{WD}} = 3.7$  for proton-transfer self-exchange between Cp(CO)<sub>3</sub>WH and its conjugate base [Cp(CO)<sub>3</sub>W<sup>-</sup>]. The stretching vibration of the W-H bond becomes translational motion in the reaction coordinate, so the zero-point energy for that degree of freedom disappears. A symmetric, linear transition state is assumed for this degenerate proton transfer, and the experimentally measured kinetic isotope effect is in excellent agreement with the value predicted by eq 3. More complicated reactions often utilize a three-center model of the transition state.<sup>2a,3</sup> Calculation of an expected kinetic isotope effect requires the input of vibrational frequencies of the transition state. Since vibrational frequencies of the transition state are not known for our hydride transfer reaction, a reliable calculation of kinetic isotope effects is not feasible, but a qualitative consideration is nevertheless informative.

Of particular interest are the decreasing  $k_{\text{MH}}/k_{\text{MD}}$  values with decreasing rate constants observed for the series of tungsten hydrides with substituted Cp ligands, culminating in the inverse isotope effect found for hydride transfer from (C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me)-(CO)<sub>3</sub>W(H/D). Inverse kinetic isotope effects were anticipated in 1949 by Bigeleisen,<sup>1a</sup> for reactions in which the transition state has higher force constants than those for the ground state; such inverse isotope effects are often associated with product-like transition states.<sup>21</sup> The force constants for stretching (and bending) vibrations are higher for C-H than for M-H bonds. Consequently, the difference in zero-point energy for M-H vs M-D is less than that for C-H vs C-D. As shown qualitatively in Figure 4,  $\Delta_{\text{CH/CD}} > \Delta_{\text{MH/MD}}$ , resulting in  $\Delta G_{\text{D}}^{\ddagger} < \Delta G_{\text{H}}^{\ddagger}$ . As indicated by the summation sign in Figure 4, this can involve more than one isotopically sensitive mode, rather than a single C-H or M-H stretching vibration. These collective differences in zero-point energy would account for the inverse isotope effect

(20) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, 109, 3945–3953.

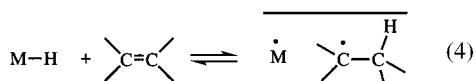
(21) Bigeleisen, J. *Pure Appl. Chem.* **1964**, 8, 217–223.



observed for hydride transfer from  $(C_5H_4CO_2Me)(CO)_3W(H/D)$ , when the transition state is sufficiently product-like to have significantly stronger force constants compared to the  $M-H/M-D$  reactants. We interpret these steadily decreasing values of  $k_{MH}/k_{MD}$  with decreasing rate constants of hydride transfer to be indicative of progressively stronger force constants of isotopically sensitive modes of the transition state, as the reaction slows down in progressing from more electron-donating Cp ligands to less-electron rich Cp ligands.

It is tempting to further conclude that the decreasing kinetic isotope effects reflect successively larger degrees of C-H bond formation (and correspondingly more M-H bond rupture) in the transition state. Such an interpretation is tenuous, however, since model calculations have shown that, for nonlinear transition states, the magnitude of the isotope effect is not highly dependent on the extent of transfer of hydrogen in the transition state.<sup>22</sup> Maximum isotope effects are expected for symmetric, linear transition states, but nonlinear transition states are known to exhibit smaller kinetic isotope effects.<sup>2b</sup> It was suggested 40 years ago that hydride transfer reactions might generally have nonlinear transition states.<sup>23</sup> Olah and co-workers reported hydride transfer reactions from the C-H bond of alkanes to a series of carbenium ions, and they strongly favored a nonlinear (i.e., triangular) three-center, two-electron transition state.<sup>24</sup> Olah's papers also called attention to the similar transition states expected in organic systems for hydride transfers to carbenium ions and for protonation of C-H (or C-C) bonds by strong acids. It has been argued<sup>17b,24</sup> that hydride transfers should favor a triangular transition state, since hydride abstracting reagents would attack the electron density in the bond (the C-H bond in organic compounds or the M-H bond for our reactions reported here), rather than the hydrogen atom itself. Calculations by Kreevoy and co-workers using a linear, three-body model for hydride transfers between carbons were, however, successful in predicting rate constants that were consistent with their experimentally measured values.<sup>6</sup> The M-H-C angle in the transition state for our hydride transfer is not known, but since even our largest  $k_{WH}/k_{WD}$  is only 1.8, a nonlinear transition state is consistent with our data.

The inverse kinetic isotope effect found experimentally is fully consistent with irreversible hydride transfer from the tungsten to carbon in a single step, and we favor this interpretation as the simplest explanation of our results. However, an alternative explanation involving equilibrium isotope effects deserves consideration. These hydride transfer reactions involve rupture of an M-H bond and formation of a C-H bond, a class of reactions for which inverse kinetic isotope effects were previously found. Hydrogenation of certain substituted styrenes and dienes by metal hydrides proceeds by hydrogen atom transfer from the metal hydride to the organic substrate (generalized in eq 4). Several metal carbonyl hydrides (Cp-



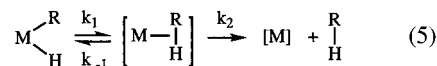
$(CO)_3WH$ ,  $Cp(CO)_3MoH$ ,  $(CO)_5MnH$ ,  $(CO)_4CoH$ ) exhibit inverse kinetic isotope effects ( $k_{MH}/k_{MD} \approx 0.4-0.7$ ) in these hydrogenations.<sup>25</sup> Inverse isotope effects ( $k_{MH}/k_{MD} \approx 0.5-0.8$ )

(22) More O'Ferrall, R. A. *J. Chem. Soc. (B)* **1970**, 785-790.

(23) Hawthorne, M. F.; Lewis, E. S. *J. Am. Chem. Soc.* **1958**, *80*, 4296-4299.

(24) (a) Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 1251-1256. (b) Olah, G. A.; Olah, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1256-1259. (c) Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 7, 1845-1851.

have also been observed in reductive elimination of alkanes from alkyl hydride complexes<sup>26</sup> (eq 5). In both of these types of



reactions, kinetic and mechanistic evidence supported the reversibility of the M-H bond cleavage/C-H bond formation steps—in eq 4 by a hydrogen atom transfer from carbon to the metal (in a caged radical pair) and in eq 5 by oxidative addition of a C-H bond to the metal in the (unobserved)  $\sigma$ -alkane complex. In both of these cases, the inverse kinetic isotope effect could therefore be due to a pre-equilibrium exhibiting an inverse equilibrium isotope effect ( $K_H/K_D < 1$ ), which is expected for reactions that form a C-H bond with a much higher stretching frequency than the stretching frequency of the M-H bond being ruptured.

All of the hydride transfers reported in this paper are thermodynamically favorable overall, but we have no data to assess partitioning of the thermodynamics between the actual hydride transfer reaction and the product-forming reaction, in which the "M<sup>+</sup>" generated by hydride transfer from MH is captured by  $BF_4^-$ . Bruno and co-workers recently measured equilibrium constants for hydride transfers to a series of substituted trityl cations in MeCN solution, which produce  $[M-NCMe]^+$  as the metal product.<sup>27</sup> Using their data in MeCN, they estimated free energies for the hydride transfers in  $CH_2Cl_2$  (eq 1). Their calculation gave  $\Delta G = -15.7$  kcal/mol for hydride transfer from  $Cp(CO)_3WH$  (eq 1).<sup>27</sup> It is therefore possible that our hydride transfer step is endothermic (particularly for the slower hydride donors), and that formation of the M-FBF<sub>3</sub> bond provides the thermodynamic driving force to make the overall reaction favorable. In changing from the substituted Cp ligands that are most electron-donating (Cp\*, indenyl) to the weakest electron donor ligand ( $C_5H_4CO_2Me$ ), the measured rate constants for hydride transfer decrease, but the thermodynamics for capture of M<sup>+</sup> by  $BF_4^-$  are likely to become even more favorable, due to decreasing electronic stabilization of M<sup>+</sup> and resultant stronger affinity for the  $BF_4^-$  ligand.

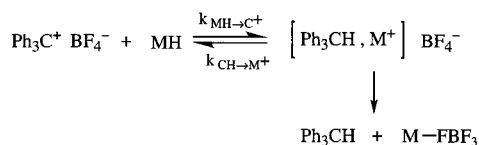
For an equilibrium to be established would require reverse hydride transfer, from CH to "M<sup>+</sup>", as shown in Scheme 1. The caged intermediate shown as  $[Ph_3CH, M^+]$  in Scheme 1 could conceivably involve an  $\eta^2$ -alkane complex with a CH bond of  $Ph_3CH$  bonded to the 16-electron M<sup>+</sup>, though the

(25) (a) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335-8337. (b) Sweany, R. L.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57-63. (c) Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886-6898. (d) Bullock, R. M.; Rappoli, B. J.; Samsel, E. G.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261-263. (e) Roth, J. A.; Wiseman, P.; Ruzsala, L. *J. Organomet. Chem.* **1983**, *240*, 271-275. (f) Ungváry, F.; Markó, L. *Organometallics* **1982**, *1*, 1120-1125. (g) Connolly, J. W. *Organometallics* **1984**, *3*, 1333-1337. (h) Wassink, B.; Thomas, M. J.; Wright, S. C.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 1995-2002. (i) Shackleton, T. A.; Baird, M. C. *Organometallics* **1989**, *8*, 2225-2232. (j) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023-2032.

(26) (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537-1550. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332-7346. (c) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897-3908. (d) Parkin, G.; Bercau, J. E. *Organometallics* **1989**, *8*, 1172-1179. (e) Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502-5504.

(27) Bruno, J. Private communication. Sarker, N.; Bruno, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 2174-2180. We thank Professor Bruno (Wesleyan University) for a preprint of his paper. For thermodynamic studies on hydride affinity of a series of substituted trityl cations as hydride acceptors, see: Zhang, X.-M.; Bruno, J. W.; Enyinnaya, E. *J. Org. Chem.* **1998**, *63*, 4671-4678.

## Scheme 1



stability of such a species might be questionable due to the steric demands of the purported  $\text{Ph}_3\text{CH}$  ligand. Another possible intermediate would be an  $\eta^2$ -arene complex of  $\text{Ph}_3\text{CH}$ , in which one of the  $\text{C}=\text{C}$  bonds of a phenyl ring bonds to the metal. A complex of this type was characterized by Sweet and Graham from hydride transfer to  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  from  $\text{Cp}(\text{CO})(\text{NO})\text{ReH}$ .<sup>28</sup> In a more general sense, organometallic complexes with hydrocarbon fragments weakly bound to a 16-electron  $\text{M}^+$  have ample precedent: Marks and co-workers have fully characterized  $\text{Cp}^*_2(\text{CH}_3)\text{Zr}^+\cdots\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$  and a series of related complexes.<sup>29</sup> We have no evidence to confirm the reversibility of hydride transfer in our reactions, but it is considered here as an explanation for the inverse isotope effect, in view of the prevalence (in reactions shown in eqs 4 and 5) of observed inverse isotope effects having their origin in reversible equilibria.

The *equilibrium* isotope effect can be estimated for the hydride transfer equilibrium. Use of eq 6 for this calculation

$$\frac{K_{\text{H}}}{K_{\text{D}}} = \exp \left\{ \frac{-hc}{2k_{\text{B}}T} \left[ \sum_i^{3N-6} (\bar{\nu}_{i(\text{CH})} - \bar{\nu}_{i(\text{CD})}) - \sum_i^{3N-6} (\bar{\nu}_{i(\text{MH})} - \bar{\nu}_{i(\text{MD})}) \right] \right\} \quad (6)$$

makes the assumption<sup>13</sup> that zero-point energy differences are the predominant influence on the equilibrium isotope effects. A complete solution of this equation would require knowledge of *all* vibrational modes of the products and reactants, but only those that are isotopically sensitive will influence the result, and we confine our consideration to stretching and bending vibrations. Stretching frequencies  $\nu(\text{M}-\text{H})$  and  $\nu(\text{M}-\text{D})$  were directly measured (Table 3), but appropriate frequencies for  $\delta(\text{M}-\text{H})$  bending modes are less well-known. Bending modes of metal hydrides normally appear in the 700–950  $\text{cm}^{-1}$  region,<sup>30,31</sup> but numerous absorptions appear in that region of the IR spectrum, so  $\delta(\text{M}-\text{H})$  bending modes are often difficult to assign. An IR and Raman spectroscopic study of  $\text{Cp}(\text{CO})_3\text{WH}$  did not locate the  $\delta(\text{W}-\text{H})$  bending modes,<sup>32</sup> but  $\delta(\text{M}-\text{H})$  bending modes were located and assigned in related metal carbonyl hydrides, 731  $\text{cm}^{-1}$  for  $(\text{CO})_5\text{MnH}$ <sup>33</sup> and 708  $\text{cm}^{-1}$  for  $(\text{CO})_4\text{CoH}$ .<sup>34</sup> A recent computational study supported these assignments and also calculated  $\delta(\text{M}-\text{H})$  bending modes for several related metal carbonyl hydrides.<sup>35</sup> We estimate 720  $\text{cm}^{-1}$  for both of the bending modes of  $\text{Cp}(\text{CO})_3\text{WH}$ . For  $\text{Ph}_3\text{CH}$ , the  $\nu(\text{C}-\text{H})$  stretch was reported<sup>36</sup> at 2878  $\text{cm}^{-1}$ . For the two degenerate  $\delta(\text{C}-\text{H})$  bending modes of  $\text{Ph}_3\text{C}-\text{H}$ , we use the

(28) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135–140.

(29) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015–10031.

(30) Jesson, J. P. Chapter 4. In *Transition Metal Hydrides*; Muettterties, E. L., Ed.; Marcel Dekker: New York, NY, 1971; pp 75–201.

(31) Sweany, R. L. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, NY, 1992; Chapter 2, pp 65–101.

(32) Davidson, G.; Duce, D. A. *J. Organomet. Chem.* **1976**, *120*, 229–237.

(33) Edgell, W. F.; Fisher, J. W.; Asato, G.; Risen, W. M., Jr. *Inorg. Chem.* **1969**, *8*, 1103–1108.

(34) Sweany, R. L.; Russell, F. N. *Organometallics* **1988**, *7*, 719–727.

(35) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1996**, *105*, 3636–3648.

values reported<sup>37</sup> in a vibrational spectral study of  $\text{Me}_3\text{C}-\text{H}$ :  $\delta(\text{C}-\text{H}) = 1330 \text{ cm}^{-1}$  (952  $\text{cm}^{-1}$  for  $\text{Me}_3\text{C}-\text{D}$ ).

Taking into account only the CH/CD and MH/MD stretching vibrations, use of eq 6 gives a calculated isotope effect of  $K_{\text{H}}/K_{\text{D}} = 0.60$ . Contributions to isotope effects resulting from changes in force constants of bending modes are often neglected<sup>2c,21</sup> in organic reactions, and this is justifiable when the transition state and reactant have comparable bending frequencies. The influence of isotopically sensitive bending modes will often have a significant influence on organometallic reactions.<sup>38</sup> Calculation of the equilibrium isotope effect for hydride transfer using the two bending modes for both CH/CD and MH/MD (in addition to the stretching modes) in eq 6 lowers the predicted equilibrium isotope effect to  $K_{\text{H}}/K_{\text{D}} = 0.18$ . Inclusion of contributions from the bending modes thus has the expected effect of making the expected equilibrium isotope effect more inverse.

## Conclusion

Kinetic isotope effects for several hydride transfers from molybdenum and tungsten hydrides to  $\text{Ph}_3\text{C}^+$  have kinetic deuterium isotope effects of  $k_{\text{MH}}/k_{\text{MD}} = 1.7$ –1.9. For a series of tungsten hydrides with systematically varied electronic effects of substituted Cp ligands, the isotope effects decrease as the rate constants for hydride transfer decrease, from a normal isotope effect of  $k_{\text{WH}}/k_{\text{WD}} = 1.8$  to an inverse isotope effect of  $k_{\text{WH}}/k_{\text{WD}} = 0.47$ . We interpret this progression of isotope effects to signal successively stronger force constants of isotopically sensitive modes of the transition state, as the reaction rate for hydride transfer decreases. The inverse isotope effect for hydride transfer from  $(\text{C}_5\text{H}_4\text{CO}_2\text{Me})(\text{CO})_3\text{W}(\text{H}/\text{D})$  is thought to be due to a product-like transition state for irreversible hydride transfer. Computational studies have been very informative for interpretation of isotope effects in other organometallic systems<sup>39</sup> and would be likely be beneficial in further interpreting our experimentally determined isotope effects.

## Experimental Section

**Sample Preparation.** All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques or in a Vacuum Atmospheres drybox. NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz for  $^1\text{H}$ ). IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. Metal hydrides were prepared as previously described.<sup>12</sup>  $\text{Cp}(\text{CO})_3\text{WD}$ ,  $\text{Cp}^*(\text{CO})_3\text{WD}$ , (indenyl)- $(\text{CO})_3\text{WD}$  (indenyl =  $\eta^5\text{-C}_9\text{H}_7$ ),  $\text{Cp}(\text{CO})_3\text{MoD}$ , and  $\text{Cp}^*(\text{CO})_3\text{MoD}$  were synthesized from their corresponding metal hydrides, by exchange with  $\text{CH}_3\text{OD}$  (99.5% D, Aldrich) at room temperature, as described previously<sup>25b</sup> for  $\text{Cp}(\text{CO})_3\text{WD}$  and  $\text{Cp}(\text{CO})_3\text{MoD}$ . The metal deuterides were purified by sublimation (isotopic purity > 94% D). THF and hexane were distilled from Na/benzophenone.

(36) Fox, J. J.; Martin, A. E. *Proc. R. Soc. (London)* **1940**, *A175*, 208–233.

(37) Evans, J. C.; Bernstein, H. J. *Can. J. Chem.* **1956**, *34*, 1037–1045.

(38) For an example where inclusion of bending modes is required to account for the observed isotope effects, see: Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353–354.

(39) (a) Computational study of the transition state for  $\text{H}_2$  addition to *trans*- $\text{IrL}_2(\text{CO})\text{X}$  complexes and relationship to kinetic isotope effects: Abu-Hasanayn, F.; Goldman, A. S.; Krogh-Jespersen, K. *J. Phys. Chem.* **1993**, *97*, 5890–5896. (b) Theoretical study of inverse equilibrium isotope effect for  $\text{H}_2/\text{D}_2$  addition to *trans*- $\text{Ir}(\text{PR}_3)_2(\text{CO})\text{X}$ : Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019–8023. (c) Experimental and theoretical study on the inverse equilibrium isotope effect for  $\text{D}_2/\text{H}_2$  binding to tungsten in  $\text{W}(\text{CO})_3(\text{PCy}_3)_2(\eta^2\text{-H}_2)$ : Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179–9190.

**Kinetics Experiments.** Procedures for sample handling, kinetics measurements, and data treatment were published earlier.<sup>12</sup> The metal hydride concentrations were typically 10–100-fold in excess of the  $\text{Ph}_3\text{C}^+$  concentration. In the case of experiments on  $\text{Cp}(\text{CO})_3\text{WH}$  and  $\text{Cp}(\text{CO})_3\text{WD}$ , the concentration of excess  $[\text{Cp}(\text{CO})_3\text{WH}(\text{D})]$  was varied from 1 to 50 mM. Reproducibility of measured rates, using the same solutions, was typically better than 2%. This does not account for uncertainties in the concentration of  $[\text{MH}]$ , due to weighing and dilution errors. As indicated in Tables 1 and 2, we estimate an overall uncertainty of  $\pm 10\%$  on the rate constants, based on reproducibility of rate data from duplicate runs with independently prepared solutions. As an indication of the reproducibility of the data, the plot shown in Figure 2 includes data points from three separately prepared solutions of  $[\text{Cp}(\text{CO})_3\text{WD}]$  and two separately prepared solutions of  $[\text{Cp}(\text{CO})_3\text{WH}]$ .

**Preparation of  $\text{Cp}(\text{CO})_2(\text{PCy}_3)\text{MoD}$ .**  $\text{Cp}(\text{CO})_2(\text{PCy}_3)\text{MoH}$ <sup>12</sup> (317 mg, 0.635 mmol) was added to a two-neck flask, which was fitted with a solid addition sidearm containing KH (35 mg, 0.872 mmol). THF (25 mL) was vacuum transferred into the flask at  $-78\text{ }^\circ\text{C}$  to give a

red-orange suspension. KH was added, the cold bath was removed, and the reaction mixture was allowed to warm to room temperature. The  $\text{Cp}(\text{CO})_2(\text{PCy}_3)\text{MoH}$  dissolved when the temperature was raised, and gas evolution was observed. The red-orange solution slowly turned to yellow. After 1.5 h, no further gas evolution was observed and  $\text{CF}_3\text{-COOD}$  ( $\sim 0.1\text{ mL}$ ,  $\sim 2$  equiv) was added. The red solution was filtered, and the volume of solvent was reduced to  $\sim 5\text{ mL}$ . Hexane (10 mL) was added, and the pale yellow precipitate was collected by filtration and washed with  $\text{CH}_3\text{OD}$  ( $5\text{ mL} \times 2$ ) and hexane (5 mL) to give  $\text{Cp}(\text{CO})_2(\text{PCy}_3)\text{MoD}$  (180 mg, 57% yield; 90% D).

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